

### SUPPORT FOR THE AMENDMENT

Support for Claims 16-20 is found in Claims 1-5 as originally presented. No new matter would be added to this application by entry of this amendment.

Upon entry of this amendment, Claims 16-20 will now be active in this application.

### REQUEST FOR RECONSIDERATION

The present invention is directed to a hair cosmetic composition.

Methods of conditioning hair to impart flexibility, smoothness and an oily feeling when the hair is wetted as well as ease of combing are sought. Conventionally used quaternary ammonium salts having long chain alkyl groups have no entirely sufficient performance when the hairs are wetted and after the hairs are dried. Furthermore, biodegradability of the product would be desirable. Accordingly, new hair cosmetic compositions are sought.

The present inventors address this problem by providing a hair cosmetic composition comprising alkoxy amide compounds of formula (I). Applicants have discovered that such alkoxy amide compounds of formula (I) provide for a hair cosmetic composition having desirable properties. Such a hair cosmetic composition is nowhere disclosed or suggested in the cited prior art of record.

The rejection of Claims 1-2 under 35 U.S.C. § 102(b) over Roncucci et al. U.S. Patent No. 4,639,468 is respectfully traversed.

Roncucci et al. fail to disclose or suggest an alkoxy amide compound of formula (I) as claimed.

Roncucci et al. describe a glycineamide compound of formula I. The glycineamide compound possesses an amine portion substituted by R and R<sup>1</sup> as well as an amide portion in which the nitrogen is substituted by groups R<sup>3</sup> and R<sup>4</sup>. In all cases, the groups R<sup>3</sup> and R<sup>4</sup> are

linear or branched **alkyl groups or phenyl**. Alkoxy substituted groups are nowhere disclosed or suggested in the reference.

In contrast, the present invention is directed to a hair cosmetic composition comprising alkoxy amide compounds of formula (I). Applicants note the claims have been amended to recite that the group  $R^1$  is of the formula  $R^5O-(AO)_n-C_mH_{2m}-$ . As the claimed compounds are directed to alkoxy amide compounds of formula (I) wherein the prior art does not describe such alkoxy substitution, the claimed invention is neither anticipated nor made obvious from this reference and accordingly withdrawal of the rejection under 35 U.S.C. § 102(b) is respectfully requested.

The rejection of Claims 1 and 2 under 35 U.S.C. § 103(a) over Kitzing et al. DD 217,513 is respectfully traversed.

Kitzing et al. fail to disclose or suggest the alkoxy amide compounds of formula (I) as claimed.

Applicants enclose herewith an English language translation of DD 217,513.

As noted by the Examiner, this reference describes the compound 2-(dimethylamino)-N-dodecyl-acetamide. The amide nitrogen is substituted with a single linear  $C_{12}$  alkyl group. Alkoxy substitution is nowhere disclosed or suggested by this reference.

In contrast, the present invention is directed to a hair cosmetic composition comprising alkoxy amide compounds of formula (I), compounds which are nowhere disclosed or suggested in the cited references. Accordingly, the present invention is not rendered obvious from this reference and accordingly withdrawal of the rejection under 35 U.S.C. § 103(a) is respectfully requested.

The rejection of Claims 1-5 under 35 U.S.C. § 103(a) over Nitsumatsu (WO98/40046) in view of Schnadel DE 1,240,872 is respectfully traversed.

Applicants enclose herewith an English language translation of DE 1,240,872.

Nitsumatsu as noted by the Examiner fails to disclose or suggest the claimed alkoxy amide compounds of formula (I). The reference to Schnadel is cited for the teaching of 2-(dimethylamino)-N-dodecyl-acetylamide. Again, the amide nitrogen is substituted by a linear C<sub>12</sub> alkyl group.

In contrast, the present invention is directed to hair cosmetic compositions comprising alkoxy amide compounds of formula (I). As the cited prior art fails to disclose or suggest a hair composition comprising alkoxy amide compounds of formula (I) as claimed, the present invention is clearly not anticipated or made obvious from these references and accordingly withdrawal of the rejections under 35 U.S.C. § 103(a) is respectfully requested.

Applicants submit this application is now in condition for allowance and early notification of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.  
Norman F. Oblon



Richard L. Chinn, Ph.D.  
Registration No. 34,305

Customer Number  
**22850**

Tel: (703) 413-3000  
Fax: (703) 413-2220  
(OSMMN 08/03)  
RLC/dbl

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CORR US 4,639,468

GERMAN DEMOCRATIC REPUBLIC

## PATENT SPECIFICATION

[logo]

(12) Industrial Patent

(19) DD (11) 217 513 A1

Issued pursuant to § 17 Paragraph 1  
Patent Act

3(51) C 07 C 103/50

OFFICE FOR INVENTIONS AND PATENTS

Published in the form filed by the Applicant

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(22) 22 April 1983

(44) 16 January 1985

(71) VEB Deutsches Hydrierwerk Rodleben, 4530 Rosslau, PO Box 140, DD

(72) Kitzing, Gerhard; Mundo, Axel, Dipl.-Chem., DD

(54) Method for synthesis of N,N-dialkylglycine amides

(57) The invention relates to a method for synthesis of N,N-dialkylglycine amides by reaction of N,N-dimethyl- or N,N-diethylaminoacetic acid and/or alkali metal salts thereof with primary and/or secondary fatty amines having an alkyl chain length of C<sub>7</sub> to C<sub>22</sub> in the presence of 0.1 to 1.1 mol of an acid, preferably hydrochloric acid, wherein the procedure is to allow the reaction components to react in aqueous medium at temperatures of 20 to 80°C and then to remove the water present in the reaction mixture and formed during the reaction from the reaction system at temperatures up to a maximum of 220°C, if necessary with passage of an inert gas. The inventive method achieves almost 100% conversion, especially when alkali metal salts of N,N-dimethylaminoacetic acid are used. The compounds synthesized according to the invention can be used in diverse ways, both as tertiary amidoamines and in the form of amine oxides, betaines and quaternary ammonium compounds that can be synthesized easily therefrom, as corrosion-protection agents, dermatological protective surfactants in cosmetics and household chemicals, active ingredients of disinfectants, bactericides, preservatives and textile auxiliaries as well as emulsifiers and adhesion agents in the construction-material and petroleum industries.

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GERMAN DEMOCRATIC REPUBLIC

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(54) Method for synthesis of N,N-dialkylglycine amides

(57) The invention relates to a method for synthesis of N,N-dialkylglycine amides by reaction of N,N-dimethyl- or N,N-diethylaminoacetic acid and/or alkali metal salts thereof with primary and/or secondary fatty amines having an alkyl chain length of C7 to C22 in the presence of 0.1 to 1.1 mol of an acid, preferably hydrochloric acid, wherein the procedure is to allow the reaction components to react in aqueous medium at temperatures of 20 to 80°C and then to remove the water present in the reaction mixture and formed during the reaction from the reaction system at temperatures up to a maximum of 220°C, if necessary with passage of an inert gas. The inventive method achieves almost 100% conversion, especially when alkali metal salts of N,N-dimethylaminoacetic acid are used. The compounds synthesized according to the invention can be used in diverse ways, both as tertiary amidoamines and in the form of amine oxides, betaines and quaternary ammonium compounds that can be synthesized easily therefrom, as corrosion-protection agents, dermatological protective surfactants in cosmetics and household chemicals, active ingredients of disinfectants, bactericides, preservatives and textile auxiliaries as well as emulsifiers and adhesion agents in the construction-material and petroleum industries.

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Re Patent No. 217513

A second publication has been issued.

(Partly confirmed pursuant to § 18 Par. 1 of the  
Act to Amend the Patent Act)

## Method for synthesis of N,N-dialkylglycine amides

### Subject matter of the invention

The subject matter of the invention is a method for direct synthesis of N,N-dialkylglycine amides, which can be used directly as tertiary aminoamides or which can be used in the form of amine oxides, betaines and quaternary ammonium compounds that can be synthesized easily therefrom, for diverse purposes, especially as corrosion-protection agents, dermatological protective surfactants in cosmetics and household chemicals, active ingredients of disinfectants, bactericides, preservatives and textile auxiliaries as well as emulsifiers and adhesion agents in the construction-material and petroleum industries.

### Characteristics of the known technical solutions

US Patent 2317999 already describes the synthesis of N,N-dimethylglycine dodecylamide from chloroacetic acid dodecylamide and dimethylamine in ethanol at 90°C to 100°C. The synthesis of the analogous compound N,N-dimethylglycine octadecylamide is the subject matter of US Patent 2256186, although the synthesis of the chloroacetic acid octadecylamide used as starting compound is not described in detail. A method widely used in industry is the synthesis of dimethylaminoacetic acid butyl ester from chloroacetic acid butyl ester and dimethylamine followed by saponification with amino compounds (Am. Soc. 62 [1940] p. 271). For the production of amino acid amides, asymmetric anhydrides, especially those of the N-acylamino acids with oxygen-containing organic or inorganic acids, have achieved paramount importance as acylating agents. For example, German Auslegeschrift [Examined Application] 1001277 describes the introduction of dialkylaminoacyl groups into amines by use of mixed anhydrides of dialkylaminocarboxylic acids and benzoic acid.

Amides of amino acids can also be obtained from what are known as Leuch's compounds, or in other words the internal anhydrides of N-carboxyl- $\alpha$ -aminocarboxylic acids (Houben Weyl, Vol. 11/2, p. 374).

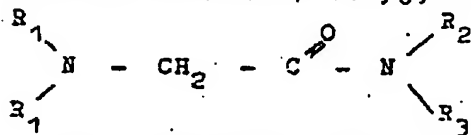
Heretofore the direct amidation of dialkylaminocarboxylic acids with primary and/or secondary fatty amines has not been described in the literature. Perhaps this may be explained by the slowly reacting ampholyte structure inherent to aminocarboxylic acids and by the fact that the relevant amidation of alkylcarboxylic acids by thermal and/or catalytic elimination of the water of reaction already leads in general only to unsatisfactory conversions and, compared with the possibilities for acylation of NH groups frequently described in the literature, was only of minor importance or hardly offered an industrial alternative.

### Object of the invention

The object of the invention is a method for synthesis of N,N-dialkylglycine amides by direct reaction of N,N-dialkylaminocarboxylic acids and/or alkali metal salts thereof by means of primary and/or secondary fatty amines, which method is technologically simple to perform and at the same time leads to high yields.

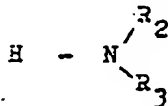
### Description of the essential features of the invention

It has been found that N,N-dialkylglycines of the general formula



in which  $R_1$  denotes  $CH_3$  or  $C_2H_5$ ,  $R_2$  denotes an alkyl group with a total carbon number of 7 to 22, and  $R_3$  denotes  $R_2$  or H,

can be synthesized very easily by direct reaction of the corresponding N,N-dialkylaminoacetic acid and/or alkali metal salts thereof with fatty amines of the formula



by allowing the reaction components first to react with one another in batches of molar size in aqueous solution at temperatures of 20°C to 80°C in the presence of 0.1 to 1.1 mol of a strong acid, preferably hydrochloric acid, the water content in the reaction mixture being 5 to 45 wt%, and then removing the water present in the reaction mixture and also that formed as a result of the amidation reaction by heating the reaction mixture to temperatures of up to 220°C, if necessary with passage of inert gases.

As already mentioned, the direct reaction of N,N-dialkylaminoacetic acid with primary and/or secondary fatty amines has not yet been developed to the point of suitability for industrial practice. One possible reason is the stable, slowly reacting ampholyte structure of the aminoacetic acids.

Surprisingly it has become possible – according to the invention by addition of acids, preferably inorganic acids – to activate these N,N-dialkylaminoacetic acids in aqueous medium and to influence their ampholytic reaction behavior in such a way that satisfactory degrees of amidation are achieved. At the same time, it has been found that almost 100% conversions are achieved if, instead of the N,N-dialkylaminoacetic acid, the alkali metal salts thereof are used in the inventive method.

The inventive method opens up the possibility of direct use of alkali metal salts of the N,N-dialkylaminoacetic acids, the synthesis of which has frequently been practiced and for many years has been carried out on a large industrial scale and, especially with respect to viewpoints of material economy and technology and to availability, represents more than merely an alternative to the traditional method of synthesis of N,N-dimethylaminoglycine alkylamides via the synthesis route of monochloroacetic acid ester to the dimethylaminoacetic acid ester.

The inventive method will be explained in more detail by means of the following examples.

#### Example 1

One mol of a 60% aqueous N,N-dimethylaminoacetic acid solution is reacted with 1 mol of dodecylamine in a reaction vessel under stirring. The water present and formed is separated via the esterification attachment at temperatures of 100°C to 180°C with constant stirring. At the end of water separation, the reaction product has a degree of amidation of 52.4%.

#### Example 2

As in Example 1, except that 0.1 mol of concentrated hydrochloric acid is also added to the reaction mixture. At the end of water separation, the degree of amidation is 70.3%.

#### Example 3

On the basis of batches of molar size, 189 g of a 70% aqueous solution of N,N-dimethylaminoacetic acid potassium salt is added together with 100.6 g of concentrated hydrochloric acid and 190 g of a primary coconut oil amine into a reaction vessel and heated to a temperature of 100°C to 180°C under stirring and separation of the water that is present and that formed by reaction.

At the end of water separation, and following removal of the formed potassium chloride by dissolution in water, the reaction product has a degree of amidation of 98.3%. Workup by distillation yields 248 g of N,N-dimethylaminoacetic acid coconut oil amide.

#### Example 4

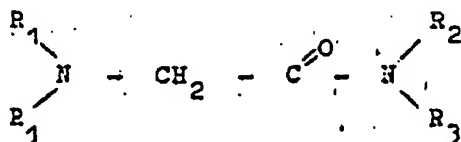
As in Example 3, except that 1 mol of tallow oil amine is used instead of coconut oil amine and separation of the water is performed by means of a constant stream of inert gas. After removal of the salt by means of hot water, the degree of amidation in the reaction product is 94.3%. Workup by distillation yields 284 g of N,N-dimethylaminoacetic acid tallow oil amide.

#### Example 5

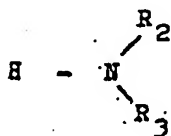
As in Example 3, except that the corresponding sodium salt is used instead of the potassium salt and the corresponding dialkylamine based on coconut oil is used instead of coconut oil amine. After removal of the sodium chloride by means of hot water, the degree of amidation in the reaction product is 93.6%.

## Claims:

1. A method for synthesis of N,N-dialkylglycine amides of the general formula



in which  $R_1$  denotes  $CH_3$  or  $C_2H_5$ ,  $R_2$  denotes an alkyl group with a total carbon number of 7 to 22, and  $R_3$  denotes  $R_2$  or H, characterized in that the corresponding N,N-dimethyl or diethylaminoacetic acid and/or alkali metal salts thereof are reacted directly with one another with fatty amines of the general formula



in such a way that the reaction components are first reacted with one another in batches of molar size in aqueous solution at temperatures of  $20^\circ C$  to  $80^\circ C$  in the presence of 0.1 to 1.1 mol of an acid, preferably hydrochloric acid, the water content in the reaction mixture being 5 to 45 wt%, and then the water present in the reaction mixture and also that formed as a result of the amidation reaction is removed by heating the reaction mixture to temperatures of up to  $220^\circ C$ , if necessary with passage of inert gases.

2. A method according to claim 1, characterized in that the salt formed during use of alkali metal salts of the N,N-dialkylaminoacetic acid remains in the reaction mixture until the end of the reaction.



FEDERAL REPUBLIC OF GERMANY

Int. Cl.:

C 07 c

C 07 d

GERMAN PATENT OFFICE

German Cl.:

12 q - 6/01

2/3

**AUSLEGESCHRIFT**

[Examined Application]

**1 240 872**

Number:

1240872

Serial No.:

H 49120 IV b/12 q

Application date:

10 May 1963

Publication date:

24 May 1967

**Method for synthesis of water-soluble, capillary-active ampholytes that can be used as detergents, cleansers and foam stabilizers**

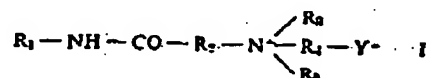
Applicant:

Henkel &amp; Cie. G.m.b.H., Düsseldorf-Holthausen, Henkelstr. 67

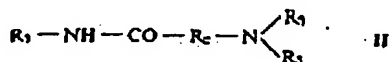
Named as inventors:

Dr. Edmund Schmadel, Dr. Alfred Kirstahler, Düsseldorf

It has been found that surface-active ampholytes of general formula I



can be obtained by quaternizing tertiary amines of general formula II



with alkylating agents containing group Y in the form of a salt or internal ester. In the above formula,  $R_1$  denotes the higher alkyl group with 8 to 20 carbon atoms that is responsible for the capillary-active properties,  $R_2$  denotes an aliphatic bridge member, especially a  $CH_2$ - group or an alkylaminoalkyl group,  $R_3$ ,  $R_4$  and  $R_5$  denote lower alkyl groups, containing at most 4 and preferably at most 3 carbon atoms, of which groups  $R_4$  and  $R_5$  can also be joined in the form of a heterocyclic ring, and  $Y^-$  denotes one of the anions  $-COO^-$  or  $-SO_3^-$ .

Synthesis of the inventive products starts from suitable fatty amines such as those accessible from fatty acids via nitriles by reduction. These fatty acids are reacted, for example, with chloroacetyl chloride to form the corresponding chloroacetyl amides, whose chlorine atom is replaced by the nitrogen atom of a suitable secondary monoamine or of a diamine or polyamine with at least one tertiary and at least one primary or secondary nitrogen atom. The compounds obtained in this way and having at least one tertiary amino group are then quaternized.

The higher alkyl groups present in the fatty amines contain 8 to 20 and preferably 12 to 18 carbon atoms. They can be straight-chain or branched and saturated or unsaturated. Such compounds can be synthesized, for example, from fatty acids of natural origin, among which fatty acid mixtures containing at least 50% of  $C_{12}$ -fatty acids are of particular practical importance. Nevertheless, synthetic fatty acids synthesized by the most diverse methods are also usable as starting materials for synthesis of the fatty amines. Such fatty acids are obtained, for example, by oxidation of paraffins or by oxidation of alcohols of the type produced, for example, by synthetic methods such as hydrogenation of carbon monoxide or the oxo synthesis using olefins. All of these fatty acids can be transformed in the process via the corresponding nitriles to the amines.

Quaternization of the tertiary amines obtained in this way can be achieved by the salts, especially alkali metal salts, of haloalkylcarboxylic acids or haloalkylsulfonic acids with 1 to 3 carbon atoms in the alkyl group, chlorine or bromine in particular being suitable halogens. Such compounds include sodium chloroacetate, sodium 2-chloropropionate and sodium 2-bromoethanesulfonate. Instead of compounds in the form of salts, there can also be used the corresponding lactones or sultones, such as  $\beta$ -propiolactone, propanesultone and butanesultone.

The inventive products are synthesized by methods known in themselves.

Since the new capillary-active substances contain both a quaternary nitrogen atom and a carboxylic acid or sulfonic acid group in the molecule, they are capable of forming internal salts which, in contrast to other types of ampholytes, dissolve in water even if they do not have the form of salts of an acid or base used exclusively for this purpose. In alkaline, neutral or acid solution, they can be used for the most diverse purposes. By virtue of their excellent skin tolerance, they are suitable as constituents of cosmetic preparations, especially as detergent substances in

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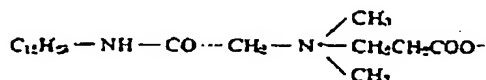
liquid, pasty or solid agents for treatment of the skin or hair.

The new ampholytes are compatible with all other capillary-active substances, regardless of whether these are anionic, cationic or nonionic products. In combination with anionic capillary-active substances, especially with products containing carboxyl groups, such as soaps, or with capillary-active sulfates or sulfonates, they exhibit a significant improvement of foaming capability and can be incorporated in all common detergents. Therein the contents are generally 1 to 50 weight per cent, preferably 1 to 10 weight per cent relative to the total quantity of those anionic capillary-active substances with which they are used in combination. Surprisingly, they have an excellent skin-protecting effect even in combination with capillary-active substances of poorer skin tolerance, as manifested by prevention of skin damage due to other capillary-active substances that are simultaneously present.

The products synthesized by using lactones or sultones are distinguished from the other products by the fact that they are obtained free of inorganic salts.

[Handwritten in Japanese: Translate this part into English]

## Example 1



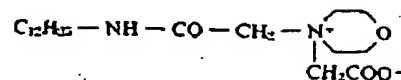
## a) Dimethylaminoacetyldodecylamine

270 g of a 25% solution of dimethylamine (1.5 mol) in ethyl alcohol was boiled under reflux for 12 hours after addition of 196.4 g of chloroacetyldodecylamine (0.75 mol). The alcohol and excess amine were then distilled off at reduced pressure. The residue was taken up in water and made alkaline with sodium hydroxide solution, after which the free amine was extracted with ether. The ether extract was dried and the ether distilled off, leaving 195.7 g of a yellow oil. Upon distillation at reduced pressure, the main fraction passed over in a quantity of 179.1 g at 164 to 167°C/0.2 mm Hg. The distillate solidified to colorless crystals having a melting point of 39 to 40°C.

## b) Quaternization of the product obtained in a)

A solution of 27.0 g (0.10 mol) of the dimethylaminoacetyldodecylamine obtained according to a) in 80 ml of ethyl alcohol was mixed with 7.2 g (0.10 mol) of  $\beta$ -propiolactone, stirred for 1 hour at room temperature and then boiled under reflux for 10 hours. The alcohol was then distilled off at reduced pressure. As residue there was obtained 33.4 g of soft colorless crystals, which were washed with acetone to remove small quantities of unreacted  $\beta$ -propiolactone. In this way there was obtained 14.1 g of colorless crystals with a melting point of 92°C. A 1% solution of the product was cloudy at room temperature and clear at 85°C; at this temperature, a pH of 5.9 was measured.

## Example 2



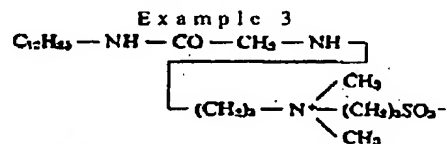
## a) Morpholinoacetyldodecylamine

A solution of 78.6 g (0.3 mol) of chloroacetyldodecylamine in 100 ml of alcohol was boiled under reflux for 12 hours after addition of 52 g (0.60 mol) of morpholine. The alcohol was then distilled off at water-pump vacuum, the resulting crystalline residue was suspended in water, the suspension was made strongly alkaline by addition of dilute sodium hydroxide solution while cooling with ice water, and the free amine was extracted with ether. The ether extract was dried and the ether distilled off, leaving 92.3 g of a brownish oil. Upon distillation at reduced pressure, the main fraction passed over at 173 to 175°C/0.1 mm Hg in a quantity of 82.2 g. The distillate solidified to yellowish crystals having a melting point of 55°C.

## b) Quaternization of the product obtained in a)

A suspension of 31.2 g (0.1 mol) of morpholinoacetyldodecylamine in 100 ml of water was mixed at 95°C under stirring with a solution of 11.65 g of sodium chloroacetate in 100 ml of water. After 20 hours of stirring at 95 to 100°C, there was obtained a clear solution, from which the dissolved sodium chloride was removed by dialysis. After concentration of the solution by evaporation, the desired product was left as a pasty substance. The pH of the 1% aqueous solution was 4.1.

## Example 3

a) N-( $\gamma$ -Dimethylaminopropyl)-aminoacetyldodecylamine

A mixture of 128.4 g (0.5 mol) of chloroacetyldodecylamine and 102.2 g (1 mol) of dimethylaminopropylamine was boiled under reflux for 2 hours, during which time the temperature in the bottoms stabilized at around 135 to 140°C. The free amine was then isolated as described in the foregoing examples. The ether extract was dried with anhydrous sodium sulfate and the ether was distilled off, leaving 135 g of a yellowish oil. Upon distillation of this oil at reduced pressure, the main fraction passed over at 182 to 192°C/0.1 mm Hg in a quantity of 85 g.

## b) Quaternization of the product obtained in a)

A solution of 32.7 g (0.10 mol) of the N-( $\gamma$ -dimethylaminopropyl)-aminoacetyldodecylamine obtained according to a) in 100 ml of alcohol was mixed dropwise at 40 to 45°C with 12.2 g (0.10 mol) of propanesultone. This mixture was then stirred for 30 minutes at room temperature and then boiled under reflux for 30 minutes. After distillation of ... [end of page]